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<b>(21) International Application Number:</b> PCT/US96/15048 <b>(22) International Filing Date:</b> 19 September 1996 (19.09.96) <b>(30) Priority Data:</b> 08/613,032 8 March 1996 (08.03.96) US <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 08/613,032 (CIP) Filed on 8 March 1996 (08.03.96) <b>(71) Applicant (for all designated States except US):</b> HUNTING INDUSTRIAL COATINGS [GB/GB]; Derby Road, Widnes, Cheshire WA8 9ND (GB). <b>(71)(72) Applicant and Inventor:</b> SAVIN, Ronald, R. [US/US]; 11001 Muirfield Drive, Rancho Mirage, CA 92270 (US). <b>(74) Agents:</b> DESHMUKH, Jayadeep, R. et al.; Dinsmore & Shohl P.L.L., 1900 Chemed Center, 255 East Fifth Street, Cincinnati, OH 45202-4797 (US).		<b>(81) Designated States:</b> AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ANTI-CORROSIVE COATING COMPOSITIONS  <b>(57) Abstract</b>  This invention provides cathodic powder coating compositions including zinc powder and/or zinc flakes without microspheres and/or graphite with a minimum conductivity when applied of 3 ohm/cm <sup>2</sup> . Specific processes are provided to allow effective manufacture of such powder coatings. A stable one package inorganic zinc-rich coating including graphite is also included.		

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## **ANTI-CORROSIVE COATING COMPOSITIONS**

5           This application is a continuation in part of co-pending U.S. Application  
Serial No. 08/613,032 filed on March 8, 1996.

### **FIELD OF THE INVENTION**

10           This invention relates generally to anti-corrosive coating compositions for  
protecting metallic substrates. A binder/vehicle and metallic zinc in various forms are  
necessary ingredients.

### **BACKGROUND OF THE INVENTION**

15           The outstanding corrosion resistance afforded by galvanizing has made it the  
most effective means for the long term protection of steel from oxidation (rusting) and  
subsequent corrosion. It is the conventional method of providing protection for  
guardrails, transmission towers, light poles, electrical equipment and dozens of other  
20       specific applications. Five mils or 125 microns of galvanizing will protect exposed  
equipment for a period in excess of 20 years. Guardrails may be coated with an  
average deposition of 75 microns and provide approximately 10 years of corrosion  
protection in an average rainfall environment. Galvanizing is applied both by hot  
dipping and electroplating, in applications where surface coatings do not provide  
25       adequate corrosion resistance.

          Galvanizing *coating* compositions, also referred to as "zinc-rich primers", are  
made from zinc metal and become oxidized only when exposed to the elements. The  
high conductivity of galvanizing compositions provides excellent cathodic protection  
30       to steel (which acts as the cathode, zinc being the anode), when exposed to a saline  
environment or other forms of oxidation caused primarily by water in its various  
forms, moisture, vapor and ice. Zinc-rich primers have been considered to be  
optimum anti-corrosion coatings on iron or steel substrates. However, certain

problems have restricted their use as industrial type primers. The action of zinc in inhibiting rust is based on an electrochemical interaction between the zinc and the steel substrate. In order *not* to insulate the zinc particles from each other and from the substrate the prior art has considered it necessary to use very little binder, with satisfactory corrosion protection achieved only when the zinc to binder ratio is at least about 9:1. The high zinc level and the relatively high density of zinc often cause undesirable settling during short term storage. Hence, the zinc is often added just prior to application and mixed rapidly during application to prevent settling and clogging of spray equipment. This deters efficient field use.

Zinc-rich primers have traditionally been limited to application over blasted and untreated steel. Passivation promotes adhesion to metal and includes the application of zinc phosphate or iron phosphate to the steel substrate. The primary reason that zinc-rich primers are rarely applied over iron phosphated steel is that these primers do not possess sufficient conductivity to provide cathodic protection to iron phosphated steel.

U.S. Patent 3,998,771, issued December, 1976 to T. J. Feneis, Jr. et al. discloses water-based coating compositions for application on iron supports to obtain anti-corrosive coatings. Single phase compositions in this patent include about 2% to 10% by weight of a non-volatile liquid epoxy resin, with low viscosity, derived from bisphenol A and an epihalohydrin, e.g., epichlorohydrin; about 2% to 10% by weight of a modified polyamide, i.e., an addition product of a water soluble polyamide and a liquid epoxy resin; and about 55% to 70% by weight of a zinc pigment having an average particle size of about 2 to 15 microns.

U.S. Patent 4,417,007, issued November 1983 to G. A. Salensky et al, discloses a one component composition containing from about 4% to 25% by weight epoxy or phenoxy resin binder and a polyamine hardener, about 43% to 90% by weight zinc dust, about 3% to 38% by weight  $Mn_3O_4$  fume pigment, up to 35% by weight additional pigments including pigment extenders and fillers (such as talc, clays, diatomaceous silica and silica), up to 5% by weight pigment suspension agent (such as

hydrous magnesium silicate and lecithin), and balance organic solvents. A 1:1 volume ratio of zinc dust to  $Mn_3O_4$  is preferred.

5 U.S. Patent 4,474,685, issued October 2, 1984 to N. Annis, discloses a molding composition comprising a polymeric binder and a multi-component electroconductive filler system comprising at least 2 members selected from the group consisting of particles of carbon black, graphite and conductive metals, said metals being selected from any of aluminium, copper, zinc or steel.

10 U.S. Patent 4,885,324, issued December 5, 1989 to Hegedus et al., discloses a coating for metallic or polymeric composite substrates, which may be used both as a primer and as a topcoat, comprising a 2-component aliphatic polyurethane binder, with titanium dioxide, zinc molybdate, zinc phosphate and organic zinc salt and titanium dioxide in controlled amounts. No graphite or use thereof is disclosed in this  
15 patent.

U.S. Patent 4,891,394, issued in January 1990 to the applicant of the present invention, discloses a coating composition for the protection of metallic and non-metallic substrates against environmental attack, comprising about 10% to about  
20 25% by weight of a film-forming polymer which may be epoxy resins having an epoxide value of about 250 to 2500, vinyl chloride resins copolymerized with polyisocyanates, and/or vinyl chloride resins copolymerized with melamines; about 30% to about 60% by weight particulate metallic zinc; an agent for control of electrical  
25 conductive characteristics comprising a crystalline silica having an oil absorption value of less than 20 as measured by ASTM Test D281-84, the volumetric ratio of such agent to the metallic zinc ranging from about 0.7:1 to about 1.25:1; about 2% to about 3% by weight of an agent for control of rheological characteristics comprising a pyrogenic amorphous silica having an average particle size less than about 0.012 micron; and at  
30 least one solvent compatible with the polymer.

French patent application 2,602,239, published February 19, 1988 in the name of the applicant of the present invention, discloses a two phase coating composition

containing up to 70% by weight of a powdered metal (based on the total weight of the composition after admixture), from about 2% to 30% of a film-forming polymer, about 2% to about 30% of a hardener for the polymer, at least 1.8% to 30% of an agent for control of rheological characteristics, and up to 30% by weight organic solvents. The preferred polymer is an epoxy resin having an average molecular weight of 350 to 3800. The agent for control of rheological characteristics comprises at least one pyrogenic silica and optionally at least one natural or transformation silica having an oil absorption value preferably not greater than 90 and more preferably not greater than 40. In the specific examples, pyrogenic silicas were used having average particle sizes of about 0.014 micron, about 0.007 micron and about 0.008 micron.

U.S. Patent 4,748,194, issued May 1987 to Geeck, discloses a coating composition for the protection of gas tanks, comprising a powder metal (such as zinc, cadmium, stainless steel, aluminum, alloys or mixtures thereof), a linear epoxy or phenoxy resin having a molecular weight of less than 15,000 cross-linked with a blocked isocyanide, a suspension agent, a thixotropic agent, and "active" and "inactive" organic solvents. The proportion of powdered metal present ranges from 13 to 52 parts per hundred. The suspension agent disclosed in this patent is polyethylene, and the thixotropic agent is silane-treated silicon dioxide, in amounts up to 2 parts per hundred.

United States Patent 5,098,938, issued March 1992 to R. R. Savin, discloses a coating composition similar to that of the above-mentioned U.S. Patent 4,891,394, wherein an epoxy resin film-forming binder is used, and wherein at least four different size grades of pyrogenic amorphous silicas are present within specified proportions and average particle sizes, together with a crystalline silica having an oil absorption value of less than 20 measured by ASTM Test D281-84.

Canadian Patent 2,065,828 provides a waterborne zinc-rich anti-corrosion primer which is based upon the combination of metallic zinc dust with a stable aqueous dispersion of a particular chlorinated addition copolymer. This primer can be formulated without the need for significant amounts of organic co-solvents. There

primers readily cure at ambient temperatures, allow overcoating shortly after drying, and produce films of desirable hardness, resiliency and adhesion both to the substrate and topcoat.

5 Canadian Patent 2,074,329 relates to an improved powder coating composition comprising (a) a resin, (b) a curing agent and (c) zinc, wherein the zinc is a mixture of (c1) lamellar zinc (zinc flakes) and (c2) zinc dust. It is essential for the practice of this invention that lamellar zinc is present.

10 United States Patent 5,167,701 issued December 1992 to the applicant of the present invention, discloses a one-package zinc-rich coating composition having an inorganic binder which provides protection of metallic substrates against environmental attack comprises, in volume percent: from about 55% to about 60% of an alkyl silicate solution having a solids content of about 35% to about 45% by weight; about  
15 10% to about 14% zinc dust of at least one different particle size grade; about 0.5% to about 2.5% zinc flakes; about 3% to about 6% particulate ferrophosphate; about 10% to about 17% of a particulate crystalline silica having an oil absorption value of less than 20 measured by ASTM Test D 281-84; about 1% to about 2.5% of at least two different size grades of pyrogenic amorphous silicas having average particle sizes  
20 ranging from about 0.007 to about 0.04 micron; about 0.3% to about 0.5% of a wetting agent; and about 7% to about 8% of an anhydrous alcohol solvent.

Zinc powder has been used only rarely in zinc-rich coating systems due to its large particle size, heavy sedimentation problems and has been ignored as an  
25 acceptable pigment. While the term "zinc powder" has been and continues to be used interchangeably with "zinc dust", as used herein "zinc powder" only means metallic zinc in granular form. As defined in a publication of the International Lead Zinc Organization, Inc.:

30 The words dust and powder have been used more or less indiscriminately in this volume to designate particulate zinc material. For the purposes of this manual, condensed zinc vapor will be termed

dust, and atomized molten zinc will be termed powder. In addition to the difference in production mode, these materials also exhibit physical differences. Whereas a particle of zinc dust is fine and spherical, that of zinc powder is coarse and irregular.

5

Preferably, the zinc powder has a particle size varying from about 20 microns to about 60 microns. Also, as discussed in German Patent 2,109,577 (discussed more below), it is known that zinc dust is covered with a zinc oxide or zinc carbonate layer which markedly depresses conductivity whereas pure zinc (as the zinc powder of the present invention), is a true metallic conductor. As used herein "zinc powder" also is different from "lamellar zinc" or "zinc flakes", as used in the Canadian Patent 2,074,329, for reasons discussed above.

10

Organic coatings made from zinc dust provide only limited protection to bare metal due to its much lower conductivity than zinc metal caused by oxidation during its manufacturing process. In conventional zinc-rich paints, the greater the conductivity the greater the area of adjacent bare steel that will be protected by the zinc metal. The level of adjacent bare metal protection is largely proportional to its conductivity measured in ohms/cm<sup>2</sup>. All galvanizing compositions, prior to exposure, will measure total conductivity of 0.00 ohm/cm<sup>2</sup> at 75 micron deposition, whereas zinc dust-rich industrial and maintenance coatings will measure from 1 to several dozen ohms/cm<sup>2</sup> at 75 microns based on the percentage of zinc dust and the particle size of the zinc dust utilized. In order to provide adequate cathodic continuity, zinc incorporated in primers customarily contains between 80-95 weight percentage of zinc dust by total weight of the zinc and the binder, not including other additives. The high percentage of zinc dust provides improved conductivity which leads to improved cathodic protection, however, the high density and low binder content causes serious problems in handling and only moderate substrate adhesion.

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Another consideration is that inorganic zinc dust-rich coating compositions are difficult to manufacture and store because of the irreversible curing mechanism triggered by exposure to moisture. Once the zinc dust has been added to a one package

30



zinc primer in the manufacturing process, the moisture curing mechanism is activated. Exposure to a minimum relative humidity of 50% effectively cures these inorganic zinc-rich coatings. Any exposure to moisture in the manufacturing or packaging process will destabilize the primer by premature curing, resulting in a product that will  
5 gel in the container in about two days. These coatings have therefore been manufactured in inert environments, using nitrogen blankets to prevent moisture contamination. One package longer shelf life zinc primer coatings have been marketed only in small volumes, since the nitrogen blanketing equipment necessary to produce such coatings in a stable form, is specialized and expensive. Despite the sensitivity to  
10 moisture, inorganic zinc-rich coating compositions continue to be the most used coatings to prevent environmental attack.

U.S. Patent 5,338,348 ("the '348 patent") discloses a coating composition for use in protecting metallic substrates from corrosion, comprising in weight percent,  
15 based on the total weight of the composition: from about 7% to 35% of film-forming substance; from about 35% to 55% of zinc powder (as defined herein); from about 5% to 25% of zinc flakes; from about 1% to 5% at least one kind of amorphous silica; and up to about 30% particulate ferrophosphate.

U.S. Patent 5,413,628 discloses a stable coating composition for use in protecting metallic substrates from corrosion, comprising in weight percent, based on the total weight of the composition: from about 7% to 35% of alkyl silicate as a film forming substance; from about 35% to 55% of zinc powder (as defined herein); from about 5% to 25% of zinc flakes; from about 0.2 to 5% of at least one amorphous  
20 silica; and up to about 30% particulate ferrophosphate; wherein the alkyl silicate comprises, in weight percent, based on the weight of the alkyl silicate: from about 5% to 20% of tetraethyl orthosilicate.

Published international application WO 96/05257 discloses a coating  
30 compositing including zinc powder and hollow, uncoated microspheres, preferably manufactured preferably using a twin screw extruder and even more preferably by feeding the zinc separately from the other ingredients.

U.S. Patent 4,014,703 to Hayati et al. discloses a vehicle composition for particulate solids comprising a condensate of an alkyl polysilicate having a silica content of about 40%, zinc chloride and an organic solvent. The vehicle composition may be mixed with a cathodically active metal and, if desired, fillers to form a coating  
5 which exhibits a high degree of stability and is highly resistant to corrosion.

U.S. Patent 4,571,268 to Frain et al. discloses a single package zinc-rich coating which comprises partially hydrolyzed ethyl silicate with large amounts of zinc dust in an organic solvent with an alkali metal nitrate as the catalyst.  
10

None of the above patents disclose a cathodic zinc-rich powder coating composition with no zinc dust, no microspheres and yet being capable of proper fluidization for electrostatic application, wherein the cured coating has a resistivity ranging from 5.50 K-ohms, where tested over a di-electric surface.  
15

None of the above patents or patent applications disclose the use of graphite in corrosion prevention coatings. The use of graphite instead of conventional pigments in conductive coatings, results in improved overall electrical conductivity; lower overall specific gravity of the coating; improved tensile strength, flexibility, corrosion resistance, and water-vapor impermeability. All of the following patents disclose such  
20 use of graphite in one way or the other.

U.S. Patent 3,838,495 issued October 1, 1974 to Kuhnert, discloses a method of forming partially or completely closed sheet metal structures having a corrosion-resistant coating surface by welding together shaped metal parts to join the structures.  
25 The coating material is said to be electrically conductive and suitable for welding. Broadly speaking, the coating material is said to have a high metal and/or graphite content and a hardenable bonding agent. Preferably, the coating material is said to contain at least 50% by weight of at least one material selected from metals and  
30 graphite. While Kuhnert allows for the use of zinc in combination with graphite, no specific example is revealed, wherein such a combination is utilized.

U.K. Patent 801,986 discloses a paint composition comprising abraded aluminum powder into which, preferably, graphite powder may also be incorporated. It is said in the patent that incorporating graphite decreased the proportion of pigmentation without destroying the electrical conductivity of the paint and improving the painting properties of the paint.

German Patent 2,101,577, published July 27, 1972 discloses a cathodic coating composition with improved electrical conductivity by at least a power of ten, by replacing part of the traditional zinc dust pigment in zinc-rich coatings by carbon pigments such as graphite and/or soot with a carbon content of at least 98% and a larger primary grain diameter. The larger the diameter, the better the electrical conductivity of the soot. Preferably, 20 to 50% by volume of the traditional zinc content is replaced by the graphite and/or soot pigments.

U.S. Patent 4,081,423, issued March 28, 1978 to Hardenfelt discloses a coating composition for producing a metallic appearance including an organic binder containing a finely divided metallic powder of a grain size not exceeding 1 mm and further including a substantial amount of powdered graphite.

J.P. 57 003,870 published January 9, 1982 to DAINIPPON PRINTING KK describes a zinc-rich paint comprising 12 to 25 weight percent of a binder consisting of tetra alkyl silicate and polyvinyl butyral, said binder having 7/3 to 2/8 of silica component in the tetra alkyl silicate, 75 to 85 weight percent zinc powder and 0.1 to 10 weight percent carbon black and/or graphite and a pigment. As the tetra alkyl silicate a prepolymer of partially hydrolyzed product of tetra ethyl orthosilicate is used.

U.S. Patent 4,545,926, issued October 8, 1985 to Fouts, Jr. et al., discloses conductive polymer compositions, comprising a polymeric material having dispersed therein conductive particles composed of a highly-conductive material and at least one particulate filler. A first particulate filler comprises a metal selected from nickel, tungsten, molybdenum, iron, chromium, aluminium, copper, solar, gold, platinum,

tantalum, zinc, cobalt, brass, tin, titanium and nichrome. A second particulate filler comprises a non-metallic conductive material such as carbon black or graphite.

5 U.S. Patent 4,996,085 to Sievers discloses a composition comprising a hardenable epoxy resin, a reinforcing filler and a specific amount of an agent such as graphite for reducing the co-efficient of friction of the composition for application to mechanical devices to reduce or prevent galling or scoring.

10 U.S. Patent 5,284,888 discloses a corrosion inhibiting, EMI/RFI shielding composition comprising a polyurethane resin which comprises a hydroxy or amine functional first polymer and an isocyanide, or isocyanurate terminated second polymer, a stabilized conductive filler, and an azole. The term "stabilized conductive filler" as used herein refers to any electrically conductive filler which has been treated such that the surfaces of the filler particles are protected from oxidation and the filler remains  
15 electrically conductive after such treatment. These stabilized fillers, when used in the coating compositions of the invention, have been found to greatly increase the resistance of the coated substrates to corrosion, especially during long term exposure to salt fog or heat, while maintaining sufficient electrical conductivity to provide EMI/RFI shielding. Fillers which may be stabilized include, but are not limited to  
20 nickel coated graphite containing fibers. The invention further provides a method of composition a substrate with a composition of the invention in order to provide EMI/RFI shielding and prevent corrosion, and a substrate thus coated. It is to be noted that by coating the graphite, this invention teaches against the use of graphite by itself.

25 In Japanese Patent Publication No. 24566/74, there is found an example of two-layer electrodeposition by electrodeposition coating. The method of this Japanese Patent Publication No. 24566/74 is concerned with a method in which using black iron oxide as an essential component and an anionic electrodeposition paint composition as a vehicle, an article to be coated is subjected to electrodeposition coating and baked to  
30 form an electrically conductive coating film with marked properties regarding adhesive strength, electrical conductivity, surface characteristics, and corrosion resistance, and a second coating layer is further provided thereon by electrodeposition coating. In

Japanese Patent Kokai (Laid-Open) No. 51958/84, in order to improve the quality of the method of the aforesaid Japanese Patent Publication No. 24566/74, a coating film as a first coating layer is formed from a combination of a cationic electrodeposition paint composition with, as an electrically conductive substance, finely divided carbon, i.e., carbon black and/or graphite, whereby uniformity of the resulting coating film and high throwing property are attained, and in order to further improve the corrosion resistance, lead compounds such as, for example, lead silicate, lead chromate, lead acetate, or lead lactate are added.

U.S. Patent 5,275,707 discloses a method of coating a metal article by forming a first electrodeposition coating layer having varistor properties on a metal article by an electrodeposition coating method by use of an electrodeposition coating film-forming composition containing from 7 to 50 parts by weight of an electrically semiconductive substance per 100 parts by weight of the solid content of the composition, and then forming a second electrodeposition coating layer on said first electrodeposition coating layer by an electrodeposition coating method by use of an anionic or cationic electrodeposition paint while applying a voltage exceeding the varistor voltage. The coating composition thus-produced has excellent varistor properties with superior corrosion resistance.

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U.S. Patent 5,275,707 discusses Japanese Patent Publication No. 24566/74 and Japanese Patent Kokai (Laid-Open) No. 51958/84 thusly:

"[I]n the case that carbon black and/or graphite which is finely divided carbon is used as an electrically conductive substance as in Japanese Patent Kokai (Laid-Open) No. 51958/84, since the electrodeposition coating is carried out by using a cationic electrodeposition paint composition but not an anionic electrodeposition paint composition, the corrosion resistance of a formed coating film is improved. However, since carbon black and/or graphite does not basically have rust resistivity, the electrodeposition paint is inferior to usual cationic electrodeposition paints free from carbon black and/or graphite in terms

of the rust resistivity, i.e., corrosion . Moreover, though it is described that in order to improve this corrosion , it is preferable to add a lead compound, there is involved a defect that in the case that an electrically conductive electrodeposition paint contains such a substance(s) in an amount necessary for attaining the generally required corrosion in cationic electrodeposition paints, the dispersion is difficult, and a uniform electrically conductive coating film is hardly obtained."

Thus, it is seen that U.S. Patent 5,275,707 teaches against the use of graphite in coating compositions because: (1) it is said to reduce rust ; (2) dispersion of coating compositions containing graphite is said to be difficult; and (3) a uniform electrically conductive coating film is not obtained.

U.S. Patent 5,213,846 discloses a corrosion resistant coating composition comprising (i) 100 parts by weight of a bisphenol type epoxy resin comprising bisphenol skeletons and epichlorohydrin skeletons and having at least two epoxy groups per molecule, said bisphenol skeletons comprising bisphenol A skeletons and bisphenol F skeletons in a weight ratio of from 95:5 to 60:40, and (ii) from 5 to 400 parts by weight of silica particles.

The steel plates treated by the coating composition of U.S. Patent 5,213,846 are likely to be subjected to welding. Therefore, it is preferred to incorporate graphite particles to the coating composition, so that a coating layer having excellent weldability will be obtained. The graphite particles are incorporated to improve the *weldability*. For this purpose, the particle size thereof is preferably at most 1  $\mu\text{m}$ . Typical commercial products of such graphite particles include, for example, Hitasol GO-102, Hitasol GP-60 and Hitasol GP-82 (tradenames, manufactured by Hitachi Funmatsu Yakin K. K.), and Supercorophite #15, Supercorophite #15Z, Supercorophite #15B, Prophite AS, Prophite W-300D, Baneyphite P-602, Baneyphite BP-4, Baneyphite BP-112, Baneyphite C-812 and Baneyphite C-9A (tradenames, manufactured by Nippon Kokuen Shoji K. K.). The graphite particles are preferably incorporated in an amount of from 0.1 to 30 parts by weight (as solid) per 100 parts by weight of the

bisphenol type epoxy resin. If the amount is less than this range, no adequate effects for improvement of the weldability will be obtained. On the other hand, if an excess amount is incorporated, processability during press processing and the corrosion tend to be low. Thus, as before, U.S. Patent 5,213,846 teaches away from using graphite if superior corrosion is desired.

U.S. Patent 5,336,303 to Cocks discloses an electrochemically active paint for cathodic protection to metallic substrates incorporating a binder, an electrochemically active metal pigment selected from magnesium, magnesium lithium alloy, magnesium aluminum alloy and calcium aluminum alloy and an electrically conductive pigment selected from carbon black and graphite, said composition further comprising a corrosion inhibiting agent selected from sodium dichromate and potassium dichromate.

U.S. Patent 4,799,959 discloses coating compositions intended to improve the characteristics of a metal substrate, especially threaded substrates. The composition incorporates at least a liquid composition containing hexavalent chromium, and a powdered metal. The composition additionally incorporates a lubricant which is solid at the temperature of use of the substrate. The invention also relates to a process for making use of these compositions and to threaded components coated in this manner.

In the compositions according to U.S. Patent 4,799,959, the solid lubricant, which is preferably a fluorinated polymer such as polytetrafluoroethylene (PTFE), MoS<sub>2</sub>, or graphite, or their mixtures, is preferably mixed with the particulate metal, but may also be packaged separately. The solid lubricant is preferably in a finely divided form, for example a powder or microspheres, and is preferably dispersed in the presence of a nonionic surface-active agent (dispersant or surfactant) such as a polyethoxy alkylphenol addition compound, for example Triton CF 54 (Rohm and Haas). This surface-active agent is employed in a quantity of between, preferably 1 to 25 grams per liter (g/l) of the total composition, preferably in the proportion of 5 to 10 g/l, because this component clearly improves the of the coatings according to the invention. This surfactant will also permit the dispersion of the various components of the composition, especially the particulate metal. The solid lubricants are employed in

quantities such that they result in concentrations by volume of on the order of 0.5 to less than 10% of the dry coating. Clearly, in this case the graphite is present as a *lubricant*.

5 U.S. Patent 4,411,742 discloses a high lubricity codeposit of zinc and graphite, and an improved method for depositing the codeposit, is disclosed. The coating is characterized by a coefficient of friction equal to or less than 0.130, and a high to corrosion evidenced by no red rust in a salt spray environment for 72 hours and no  
10 destruction due to corrosion in an industrial environment, containing sulphur dioxide, for four months. When the codeposit additionally has a chromate outer coating, the system has a coefficient of friction equal to or less than 0.112 and has no red or white rust in a salt spray environment for at least 120 hours. The codeposit is applied by immersing a cleansed metallic substrate in an acidic zinc plating electrolyte containing at least 40 g/l zinc ions and 30-110 g/l insoluble bulk graphite, with a pH of 5-5.7. The  
15 cell of which the electrolyte is a part is energized to plate out a co-deposit; the graphite is continuously agitated while in solution, the agitation being periodically interrupted to allow the graphite to settle and saturate the zinc interface as it is plating out.

U.S. Patent 4,411,742 represents the discovery that a codeposit of zinc and  
20 graphite provides an unusually good combination of physical characteristics including a coefficient of friction comparable to cadmium and, in a more particular aspect, an improved method of effectively electrodepositing zinc and graphite onto at least a vertical conductive metal surface. The codeposit is a high lubricity coating material consisting of electrocodeposited zinc and graphite uniformly distributed, the graphite  
25 being present in an amount of 30-48% by weight of the codeposit (this percentage of graphite is critical to the success of this codeposit), and the coating having a coefficient of friction equal to or less than 0.130 at a plated thickness of about 0.005 inches showing (a) no red rust in a salt spray environment for at least 72 hours, and (b) no destruction due to corrosion in an industrial environment containing sulphur dioxide  
30 after four months. It is preferable that the material have a chemically applied layer of zinc chromate at a thickness of 0.00002 inches so that optimally the coated combination will exhibit consistent torque performance at a torque load of 40 pounds,



a coefficient of friction of about 0.112 or less, and no red rust in a salt spray environment for at least 120 hours. When the codeposited coating is applied to a threaded fastener, the fastener will preferably exhibit a consistent torque tension relationship during tightening and have good solderability characteristics using either  
5 a resin solder cord or a zinc chloride containing flux.

Importantly, this patent does not contain a vehicle or a binder, and *requires* that graphite be present at a much higher level than in the present application. Importantly, the present application achieves both excellent cathodic corrosion protection and  
10 excellent flexibility and adhesion. Such flexibility and adhesion would be detrimentally affected at the high levels of graphite in the coating of U.S. Patent 4,411,742. Also, the composition of U.S. Patent 4,411,742 is "an electrolytic codeposit", whereas the present composition cannot be described as such. The addition of graphite to the zinc in the compositions of U.S. Patent 4,411,742 reduces the corrosion resistance, whereas  
15 the addition of graphite to the present composition improves corrosion resistance.

In any case, there is no disclosure or suggestion or motivation in any of the prior art documents discussed above of the desirability of a soluble graphite containing zinc-rich composition so as to decouple manufacture of the dry composition from use  
20 of the solvent.

The present application allows the solvent paint industry, a means of manufacturing solvent coatings, without the utilization of solvent prior to the manufacturing, packaging and shipment of the processed powder. Hence some of the  
25 advantages possible in powder coatings are possible by use of the present invention. Some of the advantages of Electrostatic powder coatings are: 1. Solvent-free manufacture, 2. solvent-free application, 3. recovery of over-sprayed powder, 4. no volatile organic content restrictions (VOC), 5. ease of shipment (boxes may be used, not drums), 6. reduced volume (no solvent), and 7. automated heavy volume  
30 production possible, etc.

Some of the disadvantages inherent in powder coatings are: 1. high cost of laboratory manufacture and application equipment for moving-line production, 2. powder coatings cannot be applied for maintenance, flow, coat, dip coil and numerous other applications, therefore, this technology constitutes only approximately 10% of the coatings industry total volume, and 3. as primers typically require about 45 weight percent pigment, because of their pigment volume concentration, for effective corrosion resistance, powder primers are virtually non-existent as 45% pigment will not melt on hot metal. This is because zinc powder has zero oil absorption, thereby not permitting compositions containing high volumes of zinc powder (up to about 50%), to be extruded and melted easily.

The present invention, by retaining the advantages inherent in powder processing, while allowing the onsite mixing of the compositions of the present invention with solvents, effectively removes the above-listed disadvantages associated with powder coatings technology. Thus, the present invention affords benefits of both technologies, namely powder coatings and solvent-based non-powder technologies.

### SUMMARY OF THE INVENTION

It is a primary object of the present invention to provide a dry composition including a binder, a zinc-containing substance and graphite, wherein said dry composition is easily dissolved in a solvent at a site remote from the manufacturing site of the dry composition so as to decouple the dry composition manufacture from use of the solvent.

It is an object of the present invention to provide a low-cost cathodic coating composition having enhanced corrosion protection properties, comprising graphite powder.

It is an object of the present invention to provide a graphite containing zinc-rich coating composition which overcomes the combined disadvantages of present inorganic and organic coating compositions in a cost effective manner.

It is yet another object of the present invention to provide a cathodic coating composition which delivers enhanced corrosion protection to metallic substrates susceptible to environmental attack.

5           It is a further object of the present invention to provide a zinc-rich primer that provides improved cathodic protection to treated steel with both organic and inorganic binders.

10           It is a still further object to provide a top coatable cathodic zinc-rich primer, top coatable with suitable airdry, baked, solvent, powder and water-borne topcoats.

15           It is also an object of the present invention to provide a cathodic coating composition which coating may be described as a good conductor (or which has a minimum conductivity of 3 ohms/cm<sup>2</sup>).

          It is a still further object of the present invention to provide a cathodic coating composition having greatly improved adhesion to metallic substrates as compared to conventional zinc-rich cathodic coatings.

20           It is yet another object of the present invention to provide a cathodic coating composition having greatly improved flexibility as compared to conventional zinc-rich cathodic coatings.

25           It is also an object of the present invention to provide a cathodic coating composition with enhanced water-vapor impermeability.

30           It is a primary object of the present invention to provide coating compositions with relatively low overall specific gravity, thus allowing easy fluidization, when used in the form of a powder coating.

          To achieve the foregoing and other objects, and in accordance with the first aspect of the present invention, there is provided a coating composition for use in

protecting metallic substrates from corrosion in comprising: 10-20 weight percent of a resin and curing agent/hardener/catalyst; 80-90 weight percent of a zinc powder; and wherein said composition is manufactured by feeding the zinc powder separate from the other ingredients into a twin-screw extruder and extruding the resulting mixture in said extruder.

In accordance with the second aspect of the present invention, there is provided an anti-corrosive powder coating composition comprising: 10-20 weight percent of a resin and curing agent/hardener/catalyst; 80-90% of a zinc powder; and wherein said composition is manufactured by mixing the above ingredients and extruding the same at least two times through a twin screw extruder.

In accordance with the third aspect of the present invention, there is provided an anti-corrosive coating, applied to metallic substrates as a powder, said powder comprising: 10-20 weight percent of a resin and curing agent/hardener/catalyst; 80-90 weight percent of a zinc powder; and wherein said coating has a resistivity when cured ranging from 5-50 K-ohms.

In accordance with the fourth aspect of the present invention, there is provided a coating composition comprising: from about 20 to 40 weight percent of a silicic acid ester binder as a film forming substance; from about 50% to 70% of a zinc containing substance of a zinc containing substance selected from the group consisting of zinc powder, zinc dust, and mixtures thereof; and from about 4 to 15% of graphite. Preferably about 4-10% of graphite is used, most preferably about 5%. Preferably, the zinc substance includes 10-30% zinc powder and 30-50% zinc dust.

In accordance with the fifth aspect of the present invention, there is provided an anti-corrosive powder coating comprising: 10-20 weight percent of a resin and curing agent/hardener/catalyst; 80-90 weight percent of a mixture of zinc containing substances selected from zinc dust, zinc flakes and zinc powder, wherein the zinc flakes form 5 to 15 weight percent of the entire composition; and wherein said composition is manufactured by mixing the above ingredients and extending the same

at least two times through a twin screw extruder. Preferably, about 6-9% of the flakes are present, most preferably about 7-8%. Also, most preferably the zinc dust and zinc powder are present in roughly equal proportions, ranging from 35-45% of each, the powder and dust, of the entire composition.

5

In accordance with the sixth aspect of the present invention, there is provided an anti-corrosive powder coating composition comprising: 10-20 weight percent of a resin and curing agent/hardener/catalyst; 4-15 weight percent of graphite; and 70-80 weight percent of a conductive phase selected from zinc powder, zinc dust and di-iron phosphide. Preferably, the resin itself forms about 5-15% of the entire composition, most preferably, about 9-10%. Preferably, about 4-10% of the graphite is present, most preferably about 6%. Preferably about 50-60% of the entire composition is zinc powder, the remaining conductive phase being preferably equally split between zinc dust and di-iron phosphide.

15

Therefore, the present invention provides novel and unobvious coating compositions comprising graphite for use as protection against corrosion for substrates including but not limited to: 1. Railroad rolling stock; 2. Dams, Bridges and Lift gates; 3. Storage Tanks; 4. Ships and Port Facilities; 5. Guardrails; 6. Transmission Towers; 7. Trucks, Automotive Parts and Chassis; 8. Silos and Grain Storage; 9. Light poles; 10. Gutters and Downspouts; 11. Air Conditioning Equipment; 12. Washers and Dryers; 13. Wire Fencing; 14. Ducting; 15. Corrugated Metal; 16. Pipe, Plumbing and Tubing; 17. Fasteners; 18. Steel Reinforcement Bars; and 19. Off Shore Drilling Platforms.

25

The following description provides preferred embodiments of the various aspects of this invention, simply by way of illustration, of some of the best modes contemplated for carrying out the invention. As will be realized, the invention is capable of modification in various, obvious aspects all without departing from the invention. Accordingly the description will be regarded as illustrative in nature and not restrictive.

30

### DETAILED DESCRIPTION OF THE INVENTION

Extensive testing has established that with increased cathodic continuity (conductivity) the area of adjacent bare metal protection is proportionately increased.

5 The level of protection afforded to adjacent bare metal is traditionally determined by testing the surface conductivity in ohms/cm<sup>2</sup>. In the present case, this level of protection was determined by drilling 6-8 mm holes through the coating to bare metal. This testing method reduced the testing period from thousands of hours to less than 500, thereby reducing laboratory test time. Also the method has proved to be

10 conclusive in determining the quality of bare metal protection.

The outstanding corrosion resistance of galvanized metal has made galvanizing the most effective means of long term protection of steel from oxidization and subsequent corrosion or red rust. Guardrails, transmission towers, light poles,

15 electrical equipment and hundreds of application protected by galvanizing have provided cathodic protection for periods up to twenty years. A galvanizing composition comprises essentially pure zinc metal without a binder and therefore is a superior conductor for cathodic protection and provides maximum corrosion resistance when applied over a steel substrate. Its life cycle is determined by: the level of

20 deposition and environmental factors including water (H<sub>2</sub>O) in its various forms; rain, moisture, saltfog and saltwater in addition to industrial pollutants that can considerably reduce its life cycle. The above-described performance of galvanized coatings in combating corrosion in steel substrates has caused non-galvanized coatings such as the coatings of the present invention to aspire to achieve the same or similar level of

25 protection as galvanized coatings.

To this end, coatings of the present invention (coatings of the present invention include both sprayable powder coatings, and solvent-based coatings), provide consistent cathodic conductivity throughout the primer surface producing a resistance

30 reading ranging from 5-50 K-ohms, preferably a reading of approximately 20 K-ohm when tested over a dielectric (non conductive surface), producing cathodic conductivity infinitely greater than can be measured with conventional, prior art zinc-dust

technology (organic and inorganic). When electrical resistance of approximately 20 K-ohm is achieved (as in the present invention), red rust is prevented for a period in excess of 500 hours, over a primed iron phosphated panel of cold rolled, 1000 bonderize or blasted steel subjected to a 5% NaCl saltfog (conditions equivalent to ASTM B117 saltfog exposure), with several 8 mm holes drilled through the primer. Conventional organic zinc-rich primers manufactured with zinc dust provide only limited area protection to exposed bare metal (limited to a scribed area), due to zinc dust's lower conductivity caused by oxidation during manufacture (see description above). Thus, conventional organic zinc-rich coatings with an epoxy resin as the film-forming substance (with a 90% zinc content), will develop total red rust in the drilled areas within a few days when exposed to the same environment.

The following list describes several important and unique properties achieved by the coatings of the present invention:

1. Density: The weight per gallon at equal volume solids is considerably reduced due to an effective lower zinc to binder ratio;
2. Cost: Up to a 30% lower raw material at equal volume solids;
3. Sedimentation: Soft setting is consistent throughout this development as all formulae are relatively thixotropic;
4. Application over Phosphated Steel: Without the addition of graphite, it is *impossible* to cathodically protect passivated (iron/zinc phosphated) steel. A dramatic increase in cathodic continuity and conductivity is effective in producing protective white rust to adjacent bare metal. (several 8mm holes drilled through the coating remained free of red rust in excess of 500 hours);
5. Flexibility: Organic zinc-rich formulae including powder consistently provide 160 lbs front and reverse impact resistance, an essential requirement for reinforcement bars or over coil coated or steel that is to be postformed;
6. Deposition: The thixotropic property of this development permits depositions up to 125 microns without sagging;
7. Application Properties: With the exception of the powder development all primers can be formulated for spray, brush, dip or roller coat application;
8. Ease of Recoatability: All inorganic and organic coatings of the present invention are recoatable with conventional solvent and waterborne topcoats;
9. User Friendly Inorganic Zinc primers: Manufacturing, packaging and storage of the single component moisture cured silicic acid ester development does not require a nitrogen blanket. Packaged material can be opened

and closed repeatedly without risk of gelling, a problem consistent with prior art inorganic zinc-rich primers exposed to moisture; 10. Color Development: Primers containing mostly zinc powder can be tinted to match hundreds of light and medium tone industrial primers; 11. Ease of Spot Welding: The ultra high conductivity of this development provides superior welding properties; 12. VOCs: Both the inorganic and organic primers can be formulated to achieve a VOC of 2.94 or lower; 13. Powder Application: This development is available in both epoxy and polyester primers providing exceptional anti-corrosion resistance.

10           Some of the coating compositions of this invention include powdered graphite dispersed uniformly throughout the thickness of the coating. From about 4 to 15% of graphite by weight of the total composition, preferably 4-10%, is necessary for the practice of the graphite-containing compositions of the present invention. Powdered graphite Grade No.4014 or A-99 from The Ashbury Graphite Mills, Inc., is suitable  
15           for the practice of this invention. 4014 has 95% of its weight comprised of particles between 5 and 10 microns. Graphite 625 by Carbone is a suitable alternative to 4014. The graphite content of the compositions of the present invention helps in producing resistance readings in the dried coatings of 5-50 K-ohms, preferably, approximately 20 K-ohm, when tested over a dielectric (non-conductive surface), producing cathodic  
20           conductivity infinitely greater than can be obtained with conventional zinc dust technology (organic and inorganic).

          The film forming substances of the present invention may be silicic acid ester binders, epoxy resins (powder and non-powder, including epoxy esters) and polyesters  
25           (including oil-modified polyester resins). The compositions of the present invention may be volatile-free powder coatings or volatile containing coatings.

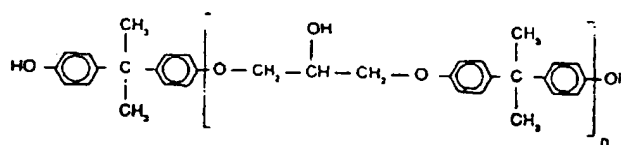
          In case of a powder coating, the presence of an antisintering agent is preferred to reduce sintering during manufacturing or storage. Amorphous silica may be  
30           produced by high temperature hydrolysis of silicon tetrachloride or by transformation of silica in an electric arc. Preferred pyrogenic amorphous silicas include those sold under the trademark "AEROSIL" by Degussa, and under the trademark "CABOSIL"



by Cabot Corporation. "AEROSIL" 300 has an average particle size of about 0.007 micron. "AEROSIL" 972 is silane treated and has an average particle size of about 0.018 micron, while "AEROSIL" 974 has an average particle size of 0.008 micron.

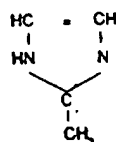
5 For the powder coating applications of the present invention, the presence of an effective amount of a curing agent/hardener/catalyst is necessary. Vestagon® B-68 by HÜLS AMERICA, Inc. and Vestagon® B-31 by HÜLS AMERICA, Inc. (both cyclic amidines), may be used as curing agents in the practice of this invention. HÜLS B-31 imparts a gloss finish to the final coating, whereas the B-68 imparts a matt finish to the final coating. D.E.H. 84 or 85 by Dow Chemical Company may also be used. D.E.H. 84 comprises 69-74% of the reaction product of an epoxy resin and bisphenol A, 24-29% bisphenol A and about 2.0% 2-methylimidazole. The chemical structures of the reaction product and of the 2-methylimidazole are given below:

15



20

2-Methylimidazole



25

D.E.H. 85 comprises 85% of the above reaction product and 15% of bisphenol A.

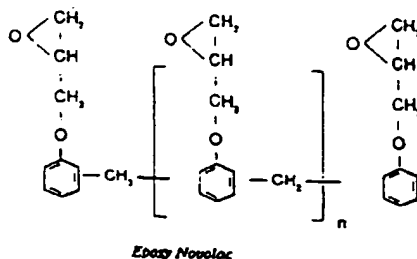
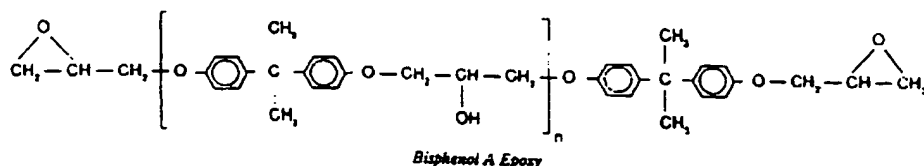
30

For a powder coating, an effective amount, preferably, 0.3-1 weight percent of a flow control agent is added. A flow control agent makes the coating generally

smoother by affecting the flow characteristics of the coating when it is in the molten state. BYK<sup>®</sup>-365 P (a polyacrylate adsorbed on silicon dioxide), by Byk-Chemie is the preferred flow control agent. For a powder coating, optionally 0.1-0.3 weight percent of an electrostatic charge modifier (preferably, "Aluminum oxide C" by DeGussa), may be post-added for ease in electrostatic spraying.

Zinc powder is available from Zinc Corporation of America (ZCA). ZCA 1239, comprising particles 95 weight percent of which are between 20 and 60 microns, is preferred. If dust is used, ZCA 1213 having a particle size 95% about 75 microns or ZCA 1222 having about 50% of its particles at about 50 microns may also be used. Most preferably, the zinc powder used, is used after passage through a 325 mesh screen. Zinc flakes are available from Novamet Specialty Products Corporation.

The film forming substance may be an epoxy powder. As is well known, epoxy resins are the reaction product of an epihalohydrin and a polyol. Shown below is the chemical structure of a bisphenol A epoxy and for an epoxy novolac.



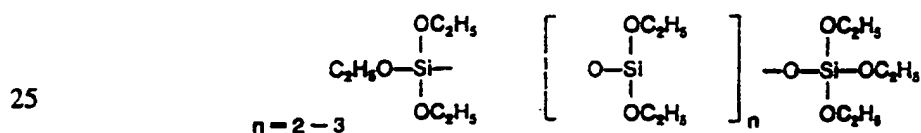
Hardening or crosslinking agents for epoxy resins include at least one compound with an -NH<sub>2</sub>, -CONH<sub>2</sub>, -NHR, -CONHR, and/or -COOH functional group, which reacts with the epoxy function. The preparation of epoxy resins and crosslinking reactions are described in United States Patent 3,954,693, issued May, 1976 to C. C. Fong, the disclosure of which is incorporated by reference. Epoxy

resins suitable for use in the present invention include those produced by Shell Chemical Company under the trademarks "EPON 3001" (modified bisphenol A/epichlorohydrin resin) and "EPON 828", and by Ciba-Geigy Co. under the trademark "488-60 Epoxy". D.E.R. 642U by Dow Chemical Company which  
 5 comprises 75-86% polymers of epoxy resin and bisphenol A and 14-25% polymers of epichlorohydrin and phenol formaldehyde novolac may also be used. Other equivalent epoxy resins are commercially available and may be used.

Preferably, the epoxy powder has an epoxide value of between 425 and 1000,  
 10 and more preferably 450-800. Even more preferably, in an epoxy powder coating composition the weight ratio of the total zinc content of the combination to the total of the zinc, the epoxy and the hardener, is at least 0.8.

Polyesters are the reaction products of poly-basic acids and polyhydric alcohols.  
 15 Oil-modified polyesters are those modified by oils or mono-basic fatty acids. Oil modified polyesters are also known as alkyds.

As to the inorganic coatings, the silicic acid ester binder comprises a substantially anhydrous composition including a hydrolyzed alkyl polysilicate such as  
 20 ethyl polysilicate, an organic solvent and catalytic amounts of alkali metal chlorides including zinc chloride, as a hardener/catalyst. The theoretical formula of ethyl polysilicate is given below:



In silicic acid ester binder based coatings, a catalytic amount of a catalyst is required so as to accelerate the reaction between the silicate, the zinc and the substrate.  
 30 The zinc chloride is present at a level ranging from 3 to 5.5 weight percent of the binder. Alternatively, and preferably, the catalyst may be an amine. The preferred silicic acid ester binders are DYNASIL S-100 and DYNASIL MKS by HÜLS. Less

preferred is DYNASIL MK 55, also by HÜLS which needs to be mixed with organic solvents and an acrylic resin solution. These binders are free of ethylene glycol monoethyl ether, a solvent with allegedly harmful health effects. Possible alternatives to this solvent include ethylene glycol propyl ether and propylene glycol propyl ether.

5      Currently, ethylene glycol monoethyl ether is used as the organic solvent in a binder composition sold by Silbond Corp. under the tradename "SILBOND" H-12A". Consequently, SILBOND" H-12A is the least preferred of all silicic acid ester binders. A description of the silicic acid ester binder component is provided in Hayati U.S. Patent 4,014,703 discussed above, which is incorporated by reference herein.

10      Tetra ethoxy silane (which has few restrictions, if any, on its use with respect to Federal, State or local environmental laws or regulations), sold by HÜLS, may be preferably used as part of the silicic acid ester binder. Tetra ethoxy silane is an inorganic solvent evaporating rapidly from the coating and is thereby very effective in helping to meet stringent new VOC standards (greater the amount of inorganic tetra ethoxy silane used

15      less volatiles are required). An effective amount of a anti-settling agent and an optimum amount of a wetting agent are preferred components of inorganic compositions of the present invention. The anti-settling agent may be amorphous silica present in an amount from about 0.5 to 1.5% by total weight of the composition and the wetting agent is Anti Terra 204 (an electroneutral solution of higher molecular

20      weight carboxylic acid salts of polyamine amides), by BYK Chemie, present in an amount from about 0.1 to 1% by total weight of the composition.

Coatings of the present invention are especially suited for use as cathodic coatings. The zinc-containing substances constitute the conductive phase and are used

25      as a "sacrificial anode". Zinc is selected because it has a more negative standard electrode potential than iron, which is the most common substrate. The zinc in the coating is thus anodic with respect to the iron. Therefore, the transformation of iron into soluble ions, which mechanism forms the gist of the corrosion phenomenon, is considerably inhibited. The zinc corrodes by forming zinc oxide and zinc carbonate,

30      which in turn further prevents corrosion. The dried film, in order to give effective cathodic protection to steel, should contain zinc in a volume such that the particles are in electrical contact.

Coatings of the present invention are prepared by mixing together the ingredients listed above or those in the specific examples. Preferably, the lighter ingredients are mixed together prior to the addition of the heavier components. In case of powder coating compositions, a two screw extruder with the capability to extrude materials of high density is preferred for obtaining optimum even distribution of the raw materials. "High density" as used herein means 1.5 to 2.5 gms/cc bulk density. The extruder used in testing the coatings of the present invention was the MP-PC™ series Powder Coatings Twin Screw Extruder by APV. It is preferred that the zinc-containing materials be fed separately from all the other raw materials. The other raw materials are preferably premixed before feeding them separate from the zinc-containing materials. Preferably, the density of the zinc containing materials (such as zinc powder) is within  $\pm 10\%$  of the density of the other raw materials. If separate feeding is used, it is desirable that the two feeders are capable of being controlled so as to add the raw materials in the correct ratio. The post-extrusion powder should preferably have a bulk (apparent) density of below 2.5 gms/cc for effective fluidization during electrostatic spraying of the powder. In order to provide optimum electrostatic conductivity during spraying and to prevent sintering, from about 0.1 to about 0.3 weight percent of electrostatic charge modifier such as aluminum oxide (preferably Alum Oxide C by Degussa), may be post-added to the extruded powder. It is important that the powder to be sprayed have a consistent bulk density. Alternative to the separate feeding, re-extrusion is recommended (extruding more than once). Partial polymerization (cross-linking) of the epoxy resin may be avoided by maintaining a low extrusion temperature. Also, cross-linking may be preferably avoided by linking the catalyst (2-methylimidazole) to less than 0.2 weight percent of the composition. Preferably the extruder is provided within a nitrogen blanket to prevent combustion due to heat buildup. The powder may then be sprayed electrostatically as is well known in the powder coatings industry. After curing in the usual manner, the coating preferably has a resistivity, when measured over a di-electric, of 5-50 K-ohms, most preferably approximately 20 K-ohms.

30

The following specific examples are given to illustrate preferred embodiments of compositions of the invention but are not to be construed as a limitation on the invention herein claimed. All percentages are by weight.

5

EXAMPLE 1

<u>Percent</u>	<u>Material</u>	<u>Manufacturer</u>
14	Polyester resin 30-3070	McWhorter
1	Curing agent Primed XL-552	Rohm & Haas
84.5	zinc powder 1222	ZCA
0.5	Aluminium Oxide "C"	Degussa

EXAMPLE 2

<u>Percent</u>	<u>Material</u>	<u>Manufacturer</u>
9.5	Epoxy Resin EPON 2012	Shell Chemical
1.0	Curing agent/catalyst DEH 84	Dow Chemical
4.5	Curing agent DEH 85	Dow Chemical
7.5	Zinc flakes	Novamet
40.0	Zinc powder (passed through 325 mesh)	ZCA
37.0	Zinc dust 15-G	Purity Zinc
5.0	Aluminium oxide (C)	Degussa

EXAMPLE 3

<u>Percent</u>	<u>Material</u>	<u>Manufacturer</u>
9.5	Epon 2012 Epoxy Resin	Shell Chemical
1.5	DEH 84 Curing agent/catalyst	Dow Chemical
4.0	DEH 85 Curing agent	Dow Chemical
6.0	Graphite 625	Ashbury Graphite
53.5	Zinc powder 1239	ZCA
12.5	Zinc dust 15-G	Purity Zinc
12.5	Di-iron phosphide Ferrophos-31	Oxy Chemicals



**EXAMPLE 4**

A single component inorganic zinc primer coating composition was prepared by mixing the constituents listed below. The quantities are in percent by weight based on the total weight:

<b><u>Percent</u></b>	<b><u>Material</u></b>	<b><u>Manufacturer</u></b>
26.0	Silicic acid ester binder (Silbond H-12A)	HÜLS
5.0	Tetra ethoxy silane	HÜLS
20.2	Zinc Powder (1239)	Zinc Corporation of America
42.0	Zinc Dust (#4)	Purity Zinc
0.9	Amorphous silica, 0.007 microns (Aerosil 300, pyrogenic silica)	Degussa
5.0	Graphite powder (A-1109)	Carbone
0.45	Wetting agent (Anti Terra 204 nonionic)	BYK Chemie
0.45	Microsieves 4A	Union Carbide

Thus, it is apparent that there have been provided, in accordance with the invention, coating compositions which fully satisfy the objects and advantages set forth above. While the invention has been described in conjunction with specific

embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations which fall within the spirit and broad scope of the appended claims.

**CLAIMS**

1. An anti-corrosive powder coating composition comprising:  
10-20 weight percent of a resin and curing agent/hardener/catalyst;  
80-90 weight percent of a zinc powder; and  
wherein said composition is manufactured by feeding the zinc powder separate  
5 from the other ingredients into a twin-screw extruder and extruding the resulting  
mixture in said extruder.
2. The powder coating composition of claim 1, wherein said zinc powder has  
95 weight percent of its particles with an average particle size of approximately 75  
microns.
3. The powder coating composition of claim 1, wherein said zinc powder has  
50 weight percent of its particles with an average particle size of approximately 50  
microns.
4. The powder coating composition of claim 1, wherein said twin-screw  
extruder is capable of extruding materials of high density.
5. The powder coating composition of claim 4, wherein said resin is a  
polyester and a curing agent is used.
6. The powder coating composition of claim 4, wherein the density of the zinc  
powder fed into said extruder is within  $\pm 10$  percent of the density of said other  
ingredients.
7. The powder coating composition of claim 6, wherein said extruder is  
provided with a nitrogen blanket to prevent combustion due to heat buildup.

8. The powder coating composition of claim 7, wherein said zinc powder and other ingredients are fed into said extruder using feeders which are capable of precisely monitoring the amount of fed materials.

9. The powder coating composition of claim 1, wherein said zinc powder is sieved through a 325 mesh screen.

10. The powder coating composition of claim 11, wherein said resin is an epoxy resin and a hardener is used.

11. An anti-corrosive powder coating composition comprising:

10-20 weight percent of a resin and curing agent/hardener/catalyst;

80-90% of a zinc powder; and

wherein said composition is manufactured by mixing the above ingredients and  
5 extruding the same at least two times through a twin screw extruder.

12. The composition of claim 11, wherein a curing agent/catalyst is used, the amount and type of curing agent/catalyst is selected so as to avoid cross-linking during the extrusion.

13. The powder coating composition of claim 11, wherein said zinc powder has 95 weight percent of its particles with an average particle size of approximately 75 microns.

14. The powder coating composition of claim 13, wherein said zinc powder has 50 weight percent of its particles with an average particle size of approximately 50 microns.

15. The powder coating composition of claim 11, wherein said twin-screw extruder is capable of extruding materials of high density.

16. The powder coating composition of claim 15, wherein said resin is a polyester and a curing agent is used.

17. The powder coating composition of claim 11, wherein said extruder is provided with a nitrogen blanket to prevent combustion due to heat buildup.

18. The powder coating composition of claim 11, wherein said zinc powder is sieved through a 325 mesh screen.

19. The powder coating compositions of claim 11, wherein said resin is an epoxy resin and a hardener is used.

20. The powder coating composition of claim 17, wherein said zinc powder and other ingredients are fed into said extruder using feeders which are capable of precisely monitoring the amount of fed materials.

21. An anti-corrosive coating, applied to metallic substrates as a powder, said powder comprising:

5 10-20 weight percent of a resin and curing agent/hardener/catalyst; 80-90 weight percent of a zinc powder; and wherein said coating has a resistivity when cured ranging from 5-50 K-ohms.

22. The powder coating composition of claim 21, wherein said zinc powder has 95 weight percent of its particles with an average particle size of approximately 75 microns.

23. The powder coating composition of claim 1, wherein said zinc powder has 50 weight percent of its particles with an average particle size of approximately 50 microns.

24. The coating of claim 21, wherein said twin-screw extruder is capable of extruding materials of high density.

25. The coating of claim 24, wherein said resin is a polyester and a curing agent is used.

26. The coating of claim 24, wherein the density of the zinc powder fed into said extruder is within  $\pm 10$  percent of the density of said other ingredients.

27. The coating of claim 21, wherein said zinc powder is sieved through a 325 mesh screen.

28. The coating of claim 27, wherein said resin is an epoxy resin and a hardener is used.

29. The coating of claim 21, wherein said powder is manufactured by feeding the zinc powder separate from the other ingredients into a twin-screw extruder and extruding the resulting mixture in said extruder.

30. The coating of claim 21, wherein said powder is manufactured by mixing the ingredients and extruding the mixture so obtained at least two times through a twin-screw extrusion.

31. The coating of claim 21, wherein a curing agent/catalyst is used, the amount and type of curing agent/catalyst is selected so as to avoid cross-linking during the extrusion.

32. The coating of claim 29 or 30, wherein said extruder is provided within a nitrogen blanket to prevent combustion due to heat buildup.

33. The coating of claim 29 or 30, wherein said zinc powder and other ingredients are fed into said extruder using feeders which are capable of precisely monitoring the amount of fed materials.

34. A coating composition comprising:  
from about 20 to 40 weight percent of an silicic acid ester binder as a film  
forming substance;  
from about 50% to 70% of a zinc containing substance of a zinc containing  
substance selected from the group consisting of zinc powder, zinc dust, and  
mixtures thereof;  
from about 4 to 15% of graphite;

35. The composition of claim 34 further comprising: an anti-settling agent;  
and a wetting agent.

36. The coating composition of claim 35, wherein said anti-settling agent is  
amorphous silica present in an amount from about 0.5 to 1.5% by total weight of the  
composition and said wetting agent is present in an amount from about 0.1 to 1% by  
total weight of the composition.

37. The coating composition of claim 36, further comprising 0.1 to 1% of a  
material selected from microsieves, calcium oxide and mixtures thereof.

38. The coating composition of claim 34, wherein the alkyl silicate comprises,  
in weight percent, based on the weight of the alkyl silicate, from about 5% to 20% of  
tetraethyl orthosilicate.

39. An anti-corrosive powder coating comprising:  
10-20 weight percent of a resin and curing agent/hardener/catalyst;  
80-90 weight percent of a mixture of zinc containing substances selected from  
zinc dust, zinc flakes, zinc powder, and mixtures thereof, wherein the zinc  
flakes form 5 to 15 weight percent of the entire composition; and  
wherein said composition is manufactured by mixing the above ingredients and  
extruding the same at least two times through a twin screw extruder.

40. The composition of claim 39, wherein a curing agent/catalyst is used, the amount and type of curing agent/catalyst is selected so as to avoid cross-linking during the extrusion.

41. The powder coating composition of claim 39, wherein said zinc powder has 95 weight percent of its particles with an average particle size of approximately 75 microns.

42. The powder coating composition of claim 41, wherein said zinc powder has 50 weight percent of its particles with an average particle size of approximately 50 microns.

43. The powder coating composition of claim 39, wherein said twin-screw extruder is capable of extruding materials of high density.

44. The powder coating composition of claim 43, wherein said resin is a polyester and a curing agent is used.

45. The powder coating composition of claim 39, wherein said extruder is provided with a nitrogen blanket to prevent combustion due to heat buildup.

46. The powder coating composition of claim 39, wherein said zinc powder is sieved through a 325 mesh screen.

47. The powder coating compositions of claim 39, wherein said resin is an epoxy resin and a hardener is used.

48. The powder coating composition of claim 45, wherein said zinc powder and other ingredients are fed into said extruder using feeders which are capable of precisely monitoring the amount of fed materials.



49. The composition of claim 40, wherein the amount of curing agent/catalyst is held at below 0.2 weight percent.

50. The composition of claim 39, wherein said resin, curing agent/hardener/catalyst and zinc flakes are mixed, first extended and then ground, after which the zinc dust and zinc powder are added to the ground powder, said mixture then is re-extruded and ground.

51. The composition of claim 50 further comprising 6.5 weight percent of aluminium oxide.

52. An anti-corrosive powder coating composition comprising:  
10-20 weight percent of a resin and curing agent/hardener/catalyst;  
4-15 weight percent of graphite; and  
70-80 weight percent of a conductive phase selected from zinc powder, zinc dust, di-iron phosphide and mixtures thereof.

53. The composition of claim 52, wherein said zinc powder is present at a level ranging from 45 to 60 weight percent and wherein said powder is manufactured by mixing the above ingredients and extending the same at least two times through a twin screw extruder.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/15048

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C09D 5/10, 5/03

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/503, 511; 523/216, 219, 244, 424, 443, 444, 451, 457, 459, 495, 496, 514, 516, 527

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,580,907 A (SAVIN) 03 December 1996.	1-53
A	US 3,838,495 A (KUHNERT) 01 October 1974, see column 2.	1-53
A	DE 2 101 577 A (HENNING) 27 July 1972, see translation.	34-38
A	US 5,413,628 A (SAVIN) 09 May 1995, see Abstract.	35-38
A	US 5,167,701 A (SAVIN) 01 December 1992, see Abstract	34-38
Y	US 3,056,684 A (LOPATA ET AL.) 02 October 1962, see examples.	34

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

11 MARCH 1997

Date of mailing of the international search report

16 APR 1997

 Name and mailing address of the ISA/US  
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## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US96/15048

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	JP 57-3870 A (DAINIPPON PRINTING KK) 01 September 1982, see Abstract.	34-36, 38, 52 ----- 1-4, 6-9, 11-15, 17, 18, 20-24, 26-33, 37, 39, 51, 53
Y	DE 30 18 765 A1 (PULVER - LACK WEIGEL KG) 26 November 1981, see abstract.	1-53
Y	UK 801,986 A (BIRD) 24 September 1958, see columns 1-3.	1-33, 39-53
Y	US 4,197,218 A (MCKAVENEY) 08 April 1980, see columns 1- 3, line 62 and Tables 1 and 2.	52, 53
Y	US 4,381,334 A (BALK ET AL.) 26 April 1983, see columns 1- 3.	1-33, 39-51
X -- Y	US 5,098,938 A (SAVIN) 24 March 1992, see Examples 3 and 4, columns 13 and 14; also column 11, line 65 et seq.	1-33 ----- 39-51

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/15048

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/15048

### A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

252/503, 511; 523/216, 219, 244, 424, 443, 444, 451, 457, 459, 495, 496, 514, 516, 527

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

Group I - Claims 1-33 and 39-51, drawn to curable resin, curing agent hardener/catalyst, zinc powder/dust/flake and optionally Al oxide.

Group II - Claims 34-38, drawn to silicic acid ester film binder, zinc powder/dust/mixture and graphite, optionally with CaO.

Group III - Claims 51-53, drawn to curable resin, curing agent/hardener/catalyst, zinc powder/dust/di-iron phosphide and graphite.

The invention of Group I, absent graphite does not suggest the compositions of Groups II and III, which do. Nor are the inventions of Groups II and III equivalent since the silicic acid ester binder of Group II does not require a hardening agent.